

[Title of Document] Patent Application  
[Reference Number] X1021043  
[Date of Submission] December 3, 2002  
5 [Addressee] Commissioner  
The Patent Office  
[International Patent Classification] C01G 1/00  
[Inventor]  
[Address] c/o ASAHI KASEI KABUSHIKI KAISHA,  
2-1, Samejima, Fuji-shi, Shizuoka,  
10 Japan  
[Name] En-Hai SUN  
[Inventor]  
[Address] c/o ASAHI KASEI KABUSHIKI KAISHA,  
2-1, Samejima, Fuji-shi, Shizuoka,  
15 Japan  
[Name] Mutsuhiro MARUYAMA  
[Applicant]  
[Applicant's ID Number] 0 0 0 0 0 0 3 3  
[Name] ASAHI KASEI KABUSHIKI KAISHA  
20 [Position of Representative] Representative  
Director  
[Name of Representative Director] Kazumoto  
YAMAMOTO  
25 [Indication on Fee]  
[Prepayment Register Number] 011187  
[Amount of Payment] ¥21,000-  
[List of Items Filed]  
[Title of Article] Specification  
30 [Number of Article] 1  
[List of Items Filed]  
[Title of Article] Abstract  
[Number of Article] 1  
[Proof Required or not] 1 : Yes

[Kind of Document] Description

[Title of the Invention] METHOD FOR PRODUCING CUPROUS OXIDE FINE PARTICLES

[Claims]

[Claim 1] A method for producing cuprous oxide fine particles, characterized in that in obtaining cuprous oxide by reducing copper acetate with 5 hydrazine in a solution containing not less than 10% by mass of water, the hydrazine is used in an amount of 0.2-5.0 moles based on 1 mole of the copper salt.

[Claim 2] A method for producing a colloidal dispersion of cuprous oxide, characterized by 10 redispersing the cuprous oxide fine particles obtained by the method of claim 1 in an organic dispersion medium.

[Claim 3] A method for producing a colloidal dispersion of cuprous oxide according to claim 2, 15 wherein the organic dispersion medium contains one or more polyhydric alcohol in a content of not less than 10% by mass.

[Detailed Description of the Invention]

20 [0001]

[Technical Field pertinent to the Invention]

The present invention relates to a method for producing cuprous oxide fine particles utilizable as starting materials of copper compounds used for 25 pigments, catalysts, colorants and conductive pastes,

or anti-contamination coating materials.

[0002]

[Prior Art]

Methods for producing cuprous oxide fine particles include physical methods, chemical methods, etc. As the physical method, there has been known a method which comprises spraying an aqueous solution of copper nitrate in a reactor in an inert atmosphere of about 1000 °C in the form of fine droplets to reduce copper nitrate to cuprous oxide (see Non-Patent Document 1). This method has a merit of high productivity of cuprous oxide, but suffers from the problem that the particle diameter of the resulting particles is distributed in a wide range of 0.1-1.5 μm.

15 [0003]

As the chemical method utilizing a reaction in a solution, there has been known a method which comprises neutralizing an aqueous solution of copper chloride in sodium chloride with an alkali, followed by aging to obtain cuprous oxide (see Patent Document 1). This method has a merit that cuprous oxide less in impurities can be obtained, but suffers from the problem that the particle diameter of the resulting particles is larger than several μm.

25 As a method for producing cuprous oxide fine particles of less than 100 nm in particle diameter, there has been known a method which comprises heating an organic copper compound (copper-N-

nitrosophenylhydroxylamine complex) at a high temperature of about 300 °C in an inert atmosphere in the present of a protecting agent such as hexadecylamine (see Non-Patent Document 2). According 5 to this method, cuprous oxide fine particles having a small particle diameter of about 10 nm can be obtained, but since the organic copper compound of starting material, the protecting agent and the organic solvent are expensive, the resulting cuprous oxide fine 10 particles become expensive, and besides a special reactor is needed because of the reaction being carried out in an inert atmosphere.

[0004]

Moreover, as a method for producing cuprous 15 oxide fine particles of less than 100 nm in particle diameter, there has been known a method of adding water and a copper salt to a polyol solvent to carry out reduction with heating (see Non-Patent Document 3).

This method has a merit that cuprous oxide fine 20 particles of 50-100 nm can be obtained without using protecting agent in an inexpensive solvent and in an air atmosphere. However, this method has problems that expensive organic copper compound (copper acetylacetonato complex) is used as a starting 25 material, resulting in expensive cuprous oxide fine particles, and besides, as for synthesis process, the organic copper compound is once dissolved with heating, and then water necessary for reaction is post-added,

followed by further heating to a reduction temperature of organic copper, and thus the synthesis operation is complicated. Moreover, a long time is required for heating.

5           Therefore, it is desired to establish a method for producing cuprous oxide fine particles of smaller than 100 nm using inexpensive starting materials by easier reaction process.

[0005]

10           [Patent Document 1] Japanese Patent No.  
1647911

              [Non-Patent Document 1] "Journal of Material Research" (No.11, Vol.11, 1996, p.2861)

15           [Non-Patent Document 2] "Journal of American Chemical Society" (1999, Vol.121, p.11595)

              [Non-Patent Document 3] "Angewandte Chemie International edition" (2001, No.40, Vol.2, p359)

[0006]

              [Problem to be solved by the Invention]

20           The object of the present invention is to provide a method for producing cuprous oxide fine particles having a particle diameter of not more than 100 nm using inexpensive starting materials by an easy reaction process.

25           [0007]

              [Means for Solving the Problem]

              As a result of intensive research conducted by the inventors on the method for producing cuprous

oxide fine particles, the present invention has been accomplished.

That is, the present invention is as follows.

(1) A method for producing cuprous oxide  
5 fine particles, characterized in that in obtaining cuprous oxide by reducing copper acetate with hydrazine in a solution containing not less than 10% by mass of water, the hydrazine is used in an amount of 0.2-5.0 moles based on 1 mole of the copper salt.

10 (2) A method for producing a colloidal dispersion of cuprous oxide, characterized by redispersing the cuprous oxide fine particles obtained by the method of (1) in an organic dispersion medium.

(3) A method for producing a colloidal  
15 dispersion of cuprous oxide described in (2), wherein the organic dispersion medium contains one or more polyhydric alcohol in a content of not less than 10% by mass.

[0008]

20 The present invention will be explained in detail below.

The particle diameter in the present invention is a primary particle diameter measured by direct observation with an electron microscope as  
25 mentioned hereinafter.

The copper starting material used in the present invention is copper acetate. The copper acetate can be used in the form of either anhydride or

hydrate.

The amount of hydrazine used as a reducing agent is 0.2-5.0 moles, preferably 0.2-3.0, more preferably 0.9-2.0 based on 1 mole of copper acetate.

- 5 If the molar ratio of hydrazine is less than 0.2, reduction reaction proceeds slowly and particle diameter of the resulting cuprous oxide exceeds 100 nm. If the molar ratio of hydrazine exceeds 5.0, the products include not only cuprous oxide, but also
- 10 copper particles, which is not preferred.

[0009]

The concentration of hydrazine used in the present invention is not limited, and is preferably not more than 64% by mass, more preferably not less than 15 20% by mass and not more than 64% by mass from the points of reaction apparatus and simplicity of reaction.

The reaction medium used in the present invention is a solution containing not less than 10% by 20 mass of water, and may be water per se. The reaction medium used together with water is not limited, and examples thereof are alcohols, ethers, esters, nitrogen compounds or the like.

[0010]

25 It is preferred to use a solvent which dissolves copper acetate simultaneously with uniformly mixing with water because reaction proceeds uniformly. From such viewpoint, an alcohol solvent is preferred.

Examples of alcohols are methanol, ethanol, propanol, butanol, ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, glycerin, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,3-5 butanediol, 1,4-butanediol, 2,3-butanediol, pentanediol, hexanediol, octanediol, etc.

[0011]

The concentration of copper acetate is not limited, but is preferably not less than 0.01% by mass 10 and not more than 50% by mass from the point of simplicity of reaction apparatus and cost. A part of copper acetate may be undissolved in the reaction medium. If the concentration of copper acetate is less than 0.01% by mass, the yield of cuprous oxide fine 15 particles obtained in one reaction is small, and if it exceeds 50% by mass, the reaction of copper acetate with hydrazine is apt to be ununiform. The concentration is more preferably not less than 3% by mass and not more than 20% by mass from the point of 20 simplicity of reaction apparatus and cost.

[0012]

The reaction temperature in the present invention is preferably not lower than 5 °C and not higher than 85 °C, more preferably not lower than 10 °C 25 and not higher than 40 °C. If the reaction temperature is lower than 5 °C, the solvent such as water is frozen and reducing ability sometimes decreases, and if it exceeds 85 °C, there sometimes occur boiling of solvent

such as water or growing of cuprous oxide fine particles.

Cuprous oxide fine particles of not more than 100 nm in particle diameter are obtained by the present invention. The resulting particles weakly contact with each other to form a soft agglomerate, which is present as a precipitate on the bottom of the reactor after completion of reduction reaction. This precipitate can be redispersed in an organic dispersion medium, and thus cuprous oxide colloidal dispersion can be obtained. As the organic dispersion medium, there may be used alcohols, ethers, esters, nitrogen compounds, or the like, and from the point of stability of the colloidal dispersion, preferred is an organic dispersion medium containing one or more polyhydric alcohol in a content of not less than 10% by mass. If the total content of one or more polyhydric alcohol is less than 10 % by mass, stability of colloid lowers.

[0013]

The polyhydric alcohol is a compound having two or more hydroxyl groups in the molecule, and is preferably liquid. Examples thereof are ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, pentanediol, hexanediol, octanediol, etc. These polyol solvents may be used each alone or in admixture of two or more.

[0014]

For redispersing soft agglomerate of cuprous oxide fine particles in the organic dispersion medium, there may be employed a general method of dispersing powder in liquid. For example, mention may be made of 5 ultrasonic method, mixer method, three-roll method, ball mill method, etc. Generally, a plurality of these dispersing means are used in combination. These dispersion treatments may be carried out at room temperature or with heating for lowering viscosity of 10 the solvent. As for the dispersion time for obtaining cuprous oxide colloidal dispersion which depends on dispersing method, about 5 minutes is enough in the case of using, for example, ultrasonic method.

[0015]

15 Cuprous oxide fine particles of not more than 100 nm in particle diameter can be simply produced by the method of the present invention. The resulting particles have extremely small particle diameter and fusion bond with reduction by a heat treatment at a 20 relatively low temperature. Thus, a copper film of high conductivity can be produced by a heat treatment at a relatively low temperature. Furthermore, the colloidal dispersion obtained by the present invention comprises cuprous oxide fine particles uniformly 25 dispersed in a solution, and can be used as a filler for ink in drawing of ultrafine wiring by ink jet method. Moreover, the resulting particles have a large surface area, and have an effect to improve activity in

the use as catalyst.

[0016]

[Mode for Carrying Out the Invention]

Next, the present invention will be explained  
5 in detail by the examples, which do not limit the  
invention in any manner.

The particle diameter of the cuprous oxide  
fine particles is measured by observing the surface  
using a transmission electron microscope (JEM-4000FX)  
10 manufactured by JASCO Corporation and obtaining the  
average particle diameter.

That the resulting particles are cuprous  
oxide is confirmed in the following manner. Using an  
X-ray diffraction device (RIGAKU-RINT 2500)  
15 manufactured by Rigaku Co., Ltd., intense diffraction  
peaks originating in planes (111) and (200) are  
observed at 36.5° and 42.4°, respectively, and when they  
coincide with XRD pattern of cuprous oxide, the  
particles are confirmed to be cuprous oxide.

20 [0017]

[Example 1]

70 ml of purified water was added to 8 g of  
copper acetate anhydride (manufactured by Wako Pure  
Chemical Industries, Ltd.). Thereto was added 2.6 ml  
25 of 64 mass% hydrazine hydrate while stirring at 25 °C so  
as to give a molar ratio of hydrazine to copper acetate  
of 1.2, thereby to carry out the reaction to obtain  
cuprous oxide fine particles having an average particle

diameter of 20 nm. 3.0 g of the resulting cuprous oxide fine particles, 0.6 g of polyethylene glycol (having an average molecular weight of 600; manufactured by Wako Pure Chemical Industries, Ltd.) 5 and 2.4 g of diethylene glycol (manufactured by Wako Pure Chemical Industries, Ltd.) were mixed, and the mixture was subjected to dispersion treatment using a agitation defoaming machine manufactured by Keyence Corporation (HM-500) under the conditions of agitation mode of 10 minutes and defoaming mode of 5 minutes.

The resulting cuprous oxide dispersion was coated at a length of 5 cm, a width of 1 cm and a thickness of 20  $\mu\text{m}$  on a slide glass. The slide glass was put in a firing furnace, followed by deaeration by 15 a vacuum pump and flowing hydrogen gas at a flow rate of 1 liter/min. The temperature of the firing furnace was raised from room temperature to 250 °C over 1 hour, and after reaching 250 °C, heating was carried out at this temperature for further 1 hour to carry out 20 firing. After cooling, the slide glass was taken out, and the slide glass was observed to confirm that a copper coat of 10  $\mu\text{m}$  in thickness was formed. The volume resistivity of this copper coat was  $7.5 \times 10^{-6}$   $\Omega\text{cm}$ , which was a low value.

25 [0018]

[Example 2]

70 ml of purified water was added to 8 g of copper acetate anhydride (manufactured by Wako Pure

Chemical Industries, Ltd.). Thereto was added 7.8 ml of 20 mass% hydrazine hydrate while stirring at 25 °C so as to give a molar ratio of hydrazine to copper acetate of 1.1, thereby to carry out the reaction to obtain 5 cuprous oxide fine particles having an average particle diameter of 30 nm.

[0019]

[Example 3]

70 ml of purified water was added to 8 g of 10 copper acetate anhydride (manufactured by Wako Pure Chemical Industries, Ltd.). Thereto was added 1.32 ml of 64 mass% hydrazine hydrate while stirring at 25 °C so as to give a molar ratio of hydrazine to copper acetate of 0.6, thereby to carry out the reaction to obtain 15 cuprous oxide fine particles having an average particle diameter of 30 nm.

[0020]

[Example 4]

70 ml of purified water was added to 8 g of 20 copper acetate anhydride (manufactured by Wako Pure Chemical Industries, Ltd.). Thereto was added 6.5 ml of 64 mass% hydrazine hydrate while stirring at 25 °C so as to give a molar ratio of hydrazine to copper acetate of 3.0, thereby to carry out the reaction to obtain 25 cuprous oxide fine particles having an average particle diameter of 60 nm.

[0021]

[Example 5]

70 ml of purified water was added to 8 g of copper acetate anhydride (manufactured by Wako Pure Chemical Industries, Ltd.). Thereto was added 2 ml of 64 mass% hydrazine hydrate while stirring at 60 °C so as 5 to give a molar ratio of hydrazine to copper acetate of 0.9, thereby to carry out the reaction to obtain cuprous oxide fine particles having an average particle diameter of 50 nm.

[0022]

10 [Example 6]

7 ml of purified water and 63 ml of ethylene glycol were added to 8 g of copper acetate anhydride (manufactured by Wako Pure Chemical Industries, Ltd.). Thereto was added 2.0 ml of 64 mass% hydrazine hydrate 15 while stirring at room temperature of 25 °C so as to give a molar ratio of hydrazine to copper acetate of 0.9, thereby to carry out the reaction to obtain cuprous oxide fine particles having an average particle diameter of 30 nm.

20 [0023]

[Example 7]

20 ml of purified water and 50 ml of ethanol were added to 8 g of copper acetate anhydride (manufactured by Wako Pure Chemical Industries, Ltd.). 25 Thereto was added 2.4 ml of 64 mass% hydrazine hydrate while stirring at room temperature of 25 °C so as to give a molar ratio of hydrazine to copper acetate of 1.1, thereby to carry out the reaction to obtain

cuprous oxide fine particles having an average particle diameter of 30 nm.

[0024]

[Example 8]

5           One gram of the cuprous oxide fine particles obtained in Example 1 was added to 30 ml of diethylene glycol, followed by subjecting to ultrasonic dispersion for 5 minutes to prepare a colloidal dispersion of cuprous oxide. The colloidal dispersion had yellow  
10 color - reddish purple color and was stable over several days.

[0025]

[Comparative Example 1]

70 ml of purified water was added to 8 g of  
15 copper acetate anhydride (manufactured by Wako Pure Chemical Industries, Ltd.). Thereto was added 0.66 ml of 64 mass% hydrazine hydrate while stirring at room temperature of 25 °C so as to give a molar ratio of hydrazine to copper acetate of 0.3, thereby to carry  
20 out the reaction to obtain cuprous oxide fine particles having an average particle diameter of 200 nm.

[0026]

[Comparative Example 2]

70 ml of diethylene glycol was added to 8 g  
25 of copper acetate anhydride (manufactured by Wako Pure Chemical Industries, Ltd.). Thereto was added 2.6 ml of 64 mass% hydrazine hydrate while stirring at 25°C so as to give a molar ratio of hydrazine to copper acetate

of 1.2, thereby to carry out the reaction. As a result, cuprous oxide fine particles were not formed, but copper was produced.

[0027]

5 [Comparative Example 3]

10 ml of purified water was added to 0.22 g of copper chloride (manufactured by Wako Pure Chemical Industries, Ltd.). Thereto was added 50  $\mu$ l of 64 mass% hydrazine hydrate while stirring at room temperature of 10 25°C so as to give a molar ratio of hydrazine to copper chloride of 0.6, thereby to carry out the reaction. As a result, cuprous oxide fine particles were not formed, but copper was produced.

[0028]

15 [Comparative Example 4]

10 ml of purified water was added to 0.26 g of copper sulfate (manufactured by Wako Pure Chemical Industries, Ltd.). Thereto was added 50  $\mu$ l of 64 mass% hydrazine hydrate while stirring at room temperature of 20 25 °C so as to give a molar ratio of hydrazine to copper sulfate of 0.6, thereby to carry out the reaction. As a result, cuprous oxide fine particles were not formed, but copper was produced.

[0029]

25 [Advantages of the Invention]

Cuprous oxide fine particles of not more than 100 nm in particle diameter can be simply produced by the present invention. The resulting particles have a

small particle diameter and can be used as conductive filler starting materials for high density wiring.

By using a composition containing the cuprous oxide fine particles for formation of circuit pattern  
5 of printed-wiring board, for formation of conductors of various via holes or for bonding of fine parts, drawing performance of fine circuits, conductivity characteristics of the circuit patters, optical (transmission) characteristics, bond strength  
10 characteristics, etc. can be improved.

The particles obtained by the present invention have a large surface area, and have an effect to improve activity in the use as catalyst. Furthermore, the particles obtained by the present  
15 invention have extremely small particle diameter, and hence can be used as a filler for ink in drawing fine wiring by ink jet method.

[Kind of Document] Abstract

[Abstract]

[Problem] To provide a method for producing cuprous oxide fine particles of not more than 100 nm in

5 particle diameter using inexpensive starting materials by easy reaction process.

[Solving Means] A method for producing cuprous oxide fine particles, characterized in that in obtaining cuprous oxide by reducing copper acetate with hydrazine

10 in a solution containing not less than 10% by mass of water, the hydrazine is used in an amount of 0.2-5.0 moles based on 1 mole of the copper salt, and a method for producing a colloidal dispersion of cuprous oxide, characterized by redispersing the resulting cuprous

15 oxide fine particles in an organic dispersion medium.

[Selected Drawing] None